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The use of ultrasound in the determination of isobaric LLV, SLV and SLLV equilibrium data. Application to the determination of the water + Na_2SO_4 or K_2SO_4 + 2-methylpropan-2-ol systems at 101.3 kPa and boiling conditions

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Highlights

The use of ultrasound in the LLVE determination has been studied.

The ultrasound effect on LLVE and SLLVE reach is explained

A comparison between with and without ultrasound is shown.

Two examples of SLLVE experimental data systems are given.

Keywords

ultrasound, water; 2-methylpropan-2-ol; Na_2SO_4; K_2SO_4; isobaric; solid–liquid–liquid–vapor; phase diagram; extended UNIQUAC

Abstract

The importance of good dispersion and homogenization of liquid and solid phases in the determination of isobaric liquid–liquid–vapor (LLV), solid–liquid–vapor (SLV) and solid–liquid–liquid–vapor (SLLV) equilibrium data is shown by analyzing the fluctuations observed during the LLV equilibrium determination of the heterogeneous azeotrope of the water + 1-butanol and water + cyclohexane systems, explaining the causes of these fluctuations, studying how to avoid them and extending them to systems with solid phases.

The LLV, SLV and SLLV equilibrium data of systems that are easily dispersed (similar phase densities and low interfacial tension) can be determined using the traditional equipment for determination of LV equilibria. In contrast, mixtures which are difficult to homogenize require more sophisticated equipment because it is difficult to obtain good phase dispersion of the liquid

phases by mere agitation. In most cases, this type of systems could be dispersed by coupling an ultrasonic homogenizer to the boiling flask of the equipment.

This apparatus, with ultrasonic waves and modifications to control the temperature of the recirculated phases has been applied to the determination of the water + Na_2SO_4 or K_2SO_4 + 2-methylpropan-2-ol systems at 101.3 kPa and boiling conditions. Comparing both systems, the size of the LLV region is larger in the system containing Na_2SO_4. The determined experimental data of these systems were correctly predicted by the extended UNIQUAC model for electrolytes, in spite of several interaction parameters having been obtained without their experimental data.

INTRODUCTION

When designing separation processes that involve the presence of vapor phases, such as distillation, the use of accurate liquid–vapor equilibrium data is required. When the complexity and non-ideality of the mixture to be separated increases, other phases can appear as two liquid phases or several solid phases. In these cases, the use only of liquid–vapor equilibrium (LV) data is not enough to fulfill a design. Solid–liquid–vapor (SLV), liquid–liquid (LL), liquid–liquid–vapor (LLV) or solid–liquid–liquid–vapor (SLLV) equilibria are just examples of the possible new equilibria that can be present.

The determination of LL equilibrium does not necessitate sophisticated equipment. Nevertheless, to obtain isobaric LV equilibrium data, more sophisticated equipment is required. Nowadays, circulation methods with recirculation of one phase (Othmer principle) or both phases (Gillespie principle) are the most widely used, and equipment has been commercially available for many years. In this equipment, reaching the equilibrium between liquid and vapor is achieved by the agitation produced by the boiling of the mixture in the boiler of the equipment. Furthermore, in the case of recirculation of the liquid phase (Gillespie principle), reaching the equilibrium is helped by the circulation of the liquid–vapor mixture through a Cottrell pump.

However, this equipment is not useful for systems that show a LL phase split or when there are solids in the mixture. Consequently, the amount of experimental data available in the literature regarding the determination of LLV equilibrium is scarce compared to that relating to other types of equilibrium [1]. With respect to the determination of the equilibrium diagrams presenting solids with SLL and SLLV regions as mixed solvent electrolyte systems, the literature available is scarce [2]. Moreover, the relatively small amount of existing experimental data is incomplete and some contain important inconsistencies. The difficulty of these determinations is that the agitation necessary to reach equilibrium in these systems must be much greater than that provided exclusively by boiling so that the mass transfer rate between the phases is increased.

In the past, LLV, SLV and SLLV determinations were usually performed using the same pieces of equipment based on that by Gillespie or a modified version thereof. The apparatus with no modification can give better or worse equilibrium data depending on the system considered. The most common modifications to the equipment involved the introduction of mechanical agitation

in the boiling flask in addition to that already produced by the bubbling of the mixture generated by the heating system [3, 4]. This type of modification aims to produce a good phase dispersion, which increases the interfacial area between the phases. As a result, mass transfer is enhanced, which aids significantly the attainment of equilibrium.

Based on this idea, Gomis et al. [5] coupled an ultrasonic homogenizer to the boiling flask to induce dispersion of the liquid phases in order to determine the LLV equilibrium of the mixtures. This modification was performed in a commercial Labodest still from i-Fischer. This equipment has been used to determine the LLV equilibrium of many ternary systems in different research centers [5–7].

When the equilibrium diagram of a system where a solid is present is to be determined, the number of phases in contact increases. In addition to the mass transfer required to reach the equilibrium state between the liquid phases and between the liquid and the vapor, the mass transfer between the solid and the liquid phase should be enhanced. Ultrasonic waves can also be used, as shown previously [8–10]. As in the case of LLV equilibrium, the ultrasonics promote a dispersion of the phases and increase the mass transfer between them. In this particular case, the dispersion promoted by the ultrasonic waves disaggregates the solid into particles with a small effective diameter, increasing the surface/volume ratio. Consequently, all the mass transfer steps between the solid and the liquid phase are enhanced significantly due to the effect of ultrasounds.

Taking into account these experiences, a first objective of this paper was to examine how the properties of the system components affect the isobaric LLV, SLV and SLLV equilibrium determinations in order to determine under which conditions the conventional apparatus cannot be used without modifications such as the application of ultrasonic waves. To do this, the fluctuations observed during the LLV equilibrium determination of the heterogeneous azeotrope of the water + 1-butanol and water + cyclohexane systems were studied, explaining the causes of these fluctuations, analyzing how to avoid them and extending them to systems with solid phases.

In the second part, an application of the modified apparatus with ultrasound was used to determine the isobaric equilibrium diagram at boiling conditions of two ternary ATPSs (Aqueous Two-Phase Systems): water + Na_2SO_4 + 2-methylpropan-2-ol and water + K_2SO_4 + 2-methylpropan-2-ol. Although the water + 2-methylpropan-2-ol pair is completely miscible, the presence of salts can split the miscible system into two liquid phases. Finally, no SLV, LLV or SLLV equilibrium data have been found in the literature for these systems at boiling temperatures. The SL equilibrium data obtained could allow design calculations of processes such as crystallization with a mixed solvent to obtain solid Na_2SO_4 or K_2SO_4 using the salting-out effect [11]. The LL equilibrium data are necessary for extraction in ATPS systems [12] and the LV data are necessary for the final separation of the solvent by evaporation or distillation.

EXPERIMENTAL

Chemicals

The compounds were employed as purchased. Table 1 shows the purity and provenance of the compounds used. The purity of the compounds was checked by means of gas chromatography (GC). Their water content was determined by Karl Fischer titration. Water was purified by means of a combination of ultrafiltration, two reverse osmosis and ion-exchange resin steps. The conductivity of the water used reached a value lower than 2 μS/cm.

Apparatus and procedures

An all-glass dynamic still with recirculation of both phases (Gillespie principle) was used to carry out the experiments. This is a commercial device (Labodest model 602), assembled in Germany by i-Fischer Labor und Verfahrenstechnik. Different modifications, which are described later, were performed on the apparatus to carry out the different parts of the work.

In all experiments, a Pt-100 sensor was employed to measure the temperatures. The probe was connected to a PRESYS thermometer (model ST-501) having an uncertainty of 0.006 K according to the certificate of calibration (scale ITS 90 [13]). The pressure inside the equipment was controlled with a Mensor high-speed pneumatic pressure controller, Model CPC3000. A Fischer M101 control system was used to measure and control the heating power. The pressure in the still was 101.3 kPa, measured and controlled to an accuracy of 0.1 kPa.

The experimental procedures were explained in detail in previous works: LLV determination[5] and SLLV determination[2]. There, the methodology used to reach equilibrium and to sample the different phases is detailed.

Analysis of the samples

Gaseous samples were injected into the gas chromatograph through an UW Type, 6-port valve from Valco Instruments Co. The connecting tube walls were superheated with a resistance tape controlled by a potentiometer so that the vapor was unsaturated and condensation avoided. All analytical work was carried out by GC on a Shimadzu GC-14B coupled to a personal computer through the Shimadzu CLASS-VP Chromatography Data System. Separation of the components was obtained in a 2 m × 3 mm column packed with Porapak Q 80/100. The oven temperature was 453 K and the helium flow rate 40 mL/min. Detection was carried out by a thermal conductivity detector (TCD). The temperature of the detector was 473 K and the current reading on the TCD was 100 mA.

The vapor phases for the water + salt + 2-methylpropan-2-ol systems are homogeneous. Consequently, they were collected in vials after condensation of the vapor stream in the equipment. The taken samples were injected then into the gas chromatograph under the same conditions described above. For the quantitative analysis of the mixtures, the external standard method was used. Calibration lines (concentration versus chromatographic area) of standards were prepared for each compound with different concentrations and used to quantify the components of the unknown samples.

The other phase(s) were composed of a sole liquid phase, two liquid phases, a liquid and a solid salt phase, or two liquid phases and a solid phase. They were introduced into a septum cap tube and placed inside a thermostatic bath at the boiling temperature so that the phases were in the same equilibrium state as inside the equipment. The analysis of the water and alcohol in the liquid samples was carried out by GC under the same chromatograph conditions as those used for the vapor phase.

For the water + 1-butanol and water + cyclohexane systems, 1-propanol was used as internal standard when quantifying the phase composition. A known amount of 1-propanol was added to the collected liquid, which subsequently was injected directly into the chromatograph. Moreover, the addition of 1-propanol serves to avoid any phase splitting that could occur when the liquid phase changes temperature from the thermostatic bath to ambient.

For the samples with salt in dissolution, two samples from the liquid phases were collected using glass syringes heated to a temperature close to boiling to avoid precipitation of the salt. One was used for the determination of the water/alcohol ratio by chromatography and the other one for the determination of the salt content.

Taking into account that 305.6 K is the temperature at which crystalline sodium sulfate decahydrate changes forming a sulfate liquid phase and an anhydrous solid phase [14], the aqueous phase samples containing Na_2SO_4 were kept at more than 323 K to ensure that any salt that precipitated in the vials before being injected was anhydrous and so there was no change in the water/alcohol ratio in the sample to be analyzed.

To determine the salt content, another sample of the liquid phase was collected and analyzed by gravimetric determination. When the amount of salt contained in the liquid phase that remained after gravimetry was not significant, a dilution with ultrapure water was performed in the tubes containing the gravimetry's dried salt and samples from these tubes subsequently analyzed by ICP-EOS. The wavelength employed was 766.49 nm for K and 589.92 nm for Na.

THE USE OF ULTRASOUND IN LLV EQUILIBRIUM DETERMINATION

As has been shown previously, the determination of the boiling points and equilibrium compositions in mixtures where two liquid phases or one solid phase are present requires significant agitation in the boiling flask where the global mixture is placed. To explain the importance of agitation and the effects produced if this is not sufficient, experiments were carried out to determine the single LLV equilibrium point at 101.3 kPa of a heterogeneous azeotropic mixture of two different binary systems of known equilibrium behavior. The two systems chosen were water + cyclohexane and water + 1-butanol.

The isobaric Txy equilibrium diagrams of the two systems are shown in Figure 1, using the same temperature scale. Both systems are heterogeneous and consequently any water-solvent heterogeneous mixture boils at the azeotropic temperature (Tz). At that temperature, the global mixture splits into two liquid phases of composition E and F in equilibrium with a vapor of

invariant composition Z. Obviously, the two liquid conjugated phases of the binary azeotrope of the two systems have different properties; for instance, solubility, density and interfacial tension are shown in Table 2 [15–19]. In this table are also found the boiling temperatures of the pure substances and the heterogeneous azeotrope. The mutual solubilities water - cyclohexane are very low and the composition of the two liquids in equilibrium in the azeotropic mixture is very different. However, as the solubility of water in 1-butanol is large, the differences in the composition of the two liquid phases of the azeotrope is smaller and consequently the difference between the phase densities and the interfacial tension is smaller.

In order to illustrate the behavior of both systems during the determination of the LLV equilibrium in the azeotropic point at 101.3 kPa, two experiments were carried out for the system with cyclohexane and other two for the system with 1-butanol. The two experiments for each system differed in the equipment used in the determination:

a) Commercial equipment as described previously with the usual agitation in the boiling flask due to the heating and boiling of the mixture.

b) Commercial equipment as modified by Gomis et al. [20] with an ultrasonic homogenizer (Braun Labsonic P with an operating frequency of 24 kHz) coupled to the boiling flask to increase the agitation and the dispersion of the two liquid phases whose LLV equilibrium is to be determined.

For each one of the four experiments the pressure and temperature read by the apparatus were recorded continuously, as was the vapor phase composition. It was assumed that these should match the equilibrium values. Figures 2 and 3 illustrate the behavior of both systems during the determination of the LLV equilibrium with and without the use of ultrasound. Figure 2 shows the evolution of temperature versus time for the water + 1-butanol system using the same temperature scale width (1 K) as in Figure 3, where the fluctuations of the system with cyclohexane are represented. The behavior for the 1-butanol system with and without ultrasound coincides. In addition, the experimental temperature was 365.73 K, which matches the literature value [15,18].

The vapor composition of the binary azeotrope coincides with that reported in the literature, as can be seen in Table 3. However, the standard deviation was slightly higher in the experiments without the ultrasound homogenizer.

Figure 3 shows the evolution of temperature versus time for the water + cyclohexane binary. In this case, the temperatures recorded during the experiment without ultrasound oscillated greatly. The oscillations persisted throughout the experiment and, as a result, a steady state could not be reached. Applying ultrasound to this kind of system attenuates the oscillations, which leads to practically constant temperatures that coincide with their literature values [18,19].

Something similar occurred with the vapor composition of the binary azeotrope shown in Table 4. Without the ultrasonic homogenizer the composition varied considerably, as the high standard deviation suggests. The mean value of all the data analyzed is very different from literature values.

When ultrasound was used to disperse the sample, the fluctuation diminished, as the standard deviation shows, and the mean value coincides with the literature values [18].

The above results show that systems that are easily dispersed (similar phase densities and low interfacial tension) can be determined using only recirculation and the conventional agitation provided by the equipment, as in the case of the water + 1-butanol system. For this reason, easily dispersed systems can be determined with equipment based on this technique, as is the case with, for example, the one developed by Iwakabe and Kosuge [21]. In contrast, mixtures that are difficult to homogenize, such as those containing cyclohexane (different phase densities and high interfacial tension) do not attain equilibrium. Large pressure and temperature fluctuations occur as a result of the poor dispersion of the heterogeneous mixture.

The above observations and conclusions were obtained for similar proportions of the two phases in the boiling flask. In the case where there was much more aqueous than organic phase and no ultrasound applied to the boiling flask, the same phenomena as described above were observed but with larger deviations. When the dispersion in the boiling flask is poor, the organic phase in the upper layer is practically the only phase that is recirculated.

All the difficulties described so far are due to insufficient dispersion of the mixture. With ultrasound a good dispersion of the phases was achieved, which led to temperature and pressure stabilization for all the systems studied regardless of their properties. The phase dispersion does not directly affect the equilibrium but can influence the mass transfer rate between the two liquid phases, which ultimately affects the rate at which equilibrium is reached.

In determinations using the conventional equipment of systems where the observed dispersion of the liquid phases is low, the liquid mixture in the boiling flask splits cleanly into separate phases, and a clearly visible interface is formed between them. This clean separation leads to the formation of a small interfacial surface, through which only a low rate of mass transfer between phases can occur. This prevents the system from attaining stability because of the processes taking place there. Consider as an example the isobaric phase diagram for the binary mixture shown in Figure 4. Suppose that at any given moment the heterogeneous binary mixture may be found in an equilibrium state; that is, there are two liquid phases: compositions x_E and x_F, and a vapor phase, composition x_Z, at a temperature T_Z. If heat continues to be supplied to the system, and it is somehow able to remain at equilibrium, a vapor of composition x_Z will form. It follows that neither the temperature nor the compositions of the liquid phases will change as long as the global composition of the liquid mixture stays between x_E and x_F. However, this is not the case in practice where the system moves away from equilibrium as a result of the following sequence of processes as well as the characteristics of the partly miscible system: the heating and evaporation of a small amount of the organic-rich phase produces a vapor of composition x_Z that is richer in W than is the liquid organic phase. Consequently, the W content of the organic-rich phase is decreased. As a result, the composition of the organic-rich liquid phase in Figure 4 shifts from F toward G and the bubble temperature increases. This displacement is compensated by the W transfer to the organic-rich liquid phase from the water-rich phase or from the bubbles of vapor coming from the

heating of the water-rich phase. Obviously, in the water-rich phase similar effects produce the displacement of point E toward point H and a resultant increase in the bubble temperature. If the mass transfer rate between phases is large enough the changes in the composition of the liquid phases will be negligible and the bubble temperature will remain steady. But, if the phases split into two well-defined layers, the contact surface between them is small. As a result, the rate of mass interchange between the two phases is not large enough to maintain a state of equilibrium.

Comparing the water + 1-butanol and water + cyclohexane systems, whose equilibrium diagrams are shown in Figure 1, the differences between the boiling temperatures of the pure compounds and of the azeotrope are smaller for the water + 1-butanol system. Besides, the mutual solubility of the pure components is high. Therefore, the liquid saturation curve between the pure component and the liquid-phase azeotrope composition is not as steep as it is for the water + cyclohexane system. In fact, in the middle of the diagram it can be observed how large changes in the liquid composition imply only small temperature variations.

Another process that provokes instability, encountered when operating commercially available equipment based on the Gillespie principle, is a poor recirculation effect resulting from the clean separation between the liquid phases in the boiling flask. Since the phase of lower density always floats on the top of the phase of higher density, the lighter phase accumulates in the recirculation conduit and the mixing chamber. This could lead to the extreme situation where only a single phase, the heavier one, is present in the boiling flask, resulting in a state very far from equilibrium. When this situation arises, the phases mix only periodically, either by a sudden boiling of a small portion of the aqueous phase or because the lighter phase accumulated in the recirculation conduit occasionally flows back into the boiling flask. As a consequence, the composition and the temperature of the recirculation stream change abruptly. This phenomenon, including the sudden drop in temperature, can be explained using again the example of the binary mixture whose phase diagram is shown in Figure 4. Referring to this phase diagram, the heavier phase in the boiling flask and the lighter phase accumulated in the recirculation conduit, both very far from equilibrium, may be represented by points G and H. If the phases were to mix, and the global composition of the mixture were to remain between x_E and x_F, the system would tend to equilibrium, as represented by points E, F and Z. Since the equilibrium state occurs at a much lower temperature than both points G and H, only a sudden distillation would allow the system to attain the equilibrium temperature and composition. Given that this process of mixing occurs only periodically, the temperature oscillates continuously, as can be seen in the videos enclosed as Supporting Information.

ULTRASOUND AND OTHER MODIFICATIONS OF THE APPARATUS FOR THE DETERMINATION OF SLV AND SLLV EQUILIBRIA

The determination of the isobaric equilibrium at the boiling temperature when a solid is present requires a great deal of stirring of the mixture in the boiling flask in order to increase the dissolution/precipitation rate of the solid particles so that it does not take long to reach equilibrium. The application of ultrasound is the ideal method of increasing agitation as well as of

decreasing the size of solid particles, thus increasing the mass transfer rate between the different phases present.

Moreover, further modifications are needed for an accurate determination. The solubility of a solid in a liquid phase depends on the solid, the mixture of solvents and the temperature. The dependence of the solubility on temperature is an important variable to be considered. The solubilities of some salts show a high dependence with the temperature, changing substantially with only small variations in temperature. Most increase the solubility with temperature but others decrease. Moreover, the rate of dissolution of a solid in a liquid phase is usually lower than the rate of dissolution of a liquid or a vapor. In addition, a liquid phase containing a dissolved solid can remain in a supersaturated state for a long time. All these factors make reaching the equilibrium state more difficult.

Accordingly, when attempting to reach the equilibrium state in the presence of salt, the temperature is a variable that must be controlled with precision in all parts of the apparatus. When the solubility dependence of the salt with temperature is small, the still with two recirculations (Gillespie principle) containing the ultrasonic probe could be used directly in the determination of SLLV and SLV equilibria. But if the dependence of the solubility of the salt on temperature is high, it is necessary to control the temperature of the return stream of the non-vapor phases (which can contain one or two liquid phases and in some cases a solid in suspension) to avoid possible precipitations of salt, which could clog and block the return conduit or the sampling valve installed. Moreover, the concentration of dissolved salt in the samples taken in these conduits would not correspond to the concentration of salt at equilibrium.

In addition, a related problem may appear when there is no control of the temperature of the returning liquid phases. Salt precipitation implies that the salt concentration in the liquid phase reaching the mixing chamber would differ from that of equilibrium. Consequently, to reattain the equilibrium state in the boiling chamber + Cottrell pump area the salt would need to be dissolved or precipitated again. As explained previously, these mass transfer steps are slower compared to those in the LL and LV systems. The reaching of equilibrium would be hindered if the returning liquid phases have their salt concentrations changed on their way to the mixing chamber.

In order to avoid these problems, several heating systems were installed around the returning conduits, the sampling valve and the mixing chamber by including a controlled-heating electric resistance around each one. The resistance maintained the temperature of these parts of the equipment as close as possible to the equilibrium temperature of the mixture. With these modifications the returning non-vapor phases at the exit of the Cottrell pump do not change their salt concentration, aiding the reaching and maintaining of the equilibrium state, avoiding salt precipitation that could block the equipment, and ensuring that the samples collected contained the salt concentrations corresponding to equilibrium.

EQUILIBRIUM DATA FOR THE WATER + Na_2SO_4 OR K_2SO_4 + 2-METHYLPROPAN-2-OL SYSTEMS

By using the experimental apparatus with ultrasound and the modifications to maintain the temperature of mixing chamber and the tubes connecting the different parts of the equipment close to the boiling temperature, equilibrium data were determined for the water + Na_2SO_4 + 2-methylpropan-2-ol and water + K_2SO_4 + 2-methylpropan-2-ol systems at 101.3 kPa and boiling conditions. No SLV, LLV or SLLV equilibrium data have been found in the literature for these systems under these conditions, although there are LL and SL equilibrium data for the system with Na_2SO_4 at temperatures lower than boiling [22–24].

The data obtained for both systems are shown in Tables 5 and 6 and represented in Figures 5 and 6. These systems present, at boiling conditions, five different equilibrium regions: one LV region, one LLV region, two SLV regions and one SLLV region. Both systems are able to split mixtures into two liquid phases at boiling.

In both systems the data obtained follow the consistency rules when a salt is present [6]: the boiling isotherms on one side and the vapor iso-composition curves on the other side do not show crossing points between the different parametric curves.

Comparing both systems, it can be seen that the size of the LLV region is noticeably larger in the system containing Na_2SO_4. The range where the amount of K_2SO_4 is adequate to form two liquid phases is lower than in for Na_2SO_4, and the amount of salt that can be dissolved is much lower. With K_2SO_4, the aqueous phase of the SLLV region has only 1.4 mol % salt, while in the case of Na_2SO_4, the same phase is formed by 5 mol % salt. This is in accordance with the fact that the difference in composition of 2-methylpropan-2-ol between the aqueous and organic phases in the SLLV region is lower in the case of potassium (0.013 and 0.324 respectively) than of sodium (0.001 and 0.486). The more ions there are in solution the higher the salting-out effect.

The extended UNIQUAC model for electrolytes [25] was used to calculate the equilibrium diagram of each system. As an example, Figure 7 shows the results of one of them. It is important to point out that the interaction parameters used[25] had been estimated using only the SL and LL equilibria (but not LV, LLV or SLLV equilibrium data) of the water + Na_2SO_4 + 2-methylpropan-2-ol system without including data of the water + K_2SO_4 + 2-methylpropan-2-ol system, since there are no published experimental equilibrium data for this system. The interaction parameters of 2-methylpropan-2-ol with the K^+ or SO_4^{2-} ions were obtained from systems with containing these ions as other salts, i.e., KCl or Na_2SO_4. The application of these interaction parameters for the system with K_2SO_4 converts the calculation in a prediction from the equilibrium of other systems. In spite of that, the results calculated with the model are similar to the experiment, as shown in Figure 7 for the system with K_2SO_4; the boiling temperatures and the shapes of the different regions are correctly predicted by the model.

CONCLUSIONS

For the determination of LLVE data in systems with partly miscible compounds, it is important that the two liquid phases are in intimate contact with each other. There are systems whose liquid phases are easily dispersed as both phases have similar densities and low interfacial tension. These

systems can be determined using the conventional equipment for LV equilibrium determinations, since dispersion and the mass transfer between liquid phases are easily obtained.

However, most systems with partly miscible components give two liquid phases with very different phase densities and high interfacial tension; consequently, it is difficult for the mass transfer rate between them to be high enough to attain equilibrium in a short time. Large pressure and temperature fluctuations occur as a result of the poor dispersion of the heterogeneous mixture. These systems require more sophisticated equipment because it is difficult to obtain good phase dispersion of the liquid phases by mere agitation. In most cases, this type of systems could be dispersed by coupling an ultrasonic homogenizer to the boiling flask of the equipment.

In the case of SLLV or SLV equilibria, the presence of salts makes reaching equilibrium and maintaining the system in this state more difficult. The modifications to the equipment, comprised mainly of the ultrasonic probe in the boiling chamber and the addition of a temperature control system on the liquid return tube, help significantly in reaching the equilibrium state and avoiding precipitation and/or dissolution of the salts.

The equipment with the aforementioned modifications permits to obtain accurate and consistent equilibrium data when more than one solid or liquid phase apart from the vapor phase is present, such as for the water + Na_2SO_4 or K_2SO_4 + 2-methylpropan-2-ol systems at 101.3 kPa and boiling conditions. Comparing both systems, the size of the LLV region is larger in the system containing Na_2SO_4. The determined experimental data of these systems were correctly predicted by the extended UNIQUAC model for electrolytes, in spite of several interaction parameters having been obtained without their experimental data.

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Supporting Information

Four different videos are provided. The boiling flask, temperature and pressure in the apparatus have been recorded in each video for different systems:

Two videos, (1-butanol without US.mp4) and (1-butanol with US.mp4), correspond to the system water + 1-butanol without and with the ultrasound homogenizer: there are not large fluctuations in temperature and pressure regardless of whether the ultrasound probe is connected or not

The other two videos, (cyclohexane without US.mp4) and (cyclohexane with US.mp4), correspond to the binary water + cyclohexane system without and with ultrasounds: sudden boiling occurs

without ultrasounds, causing large fluctuations in pressure and temperature. When using the ultrasound homogenizer, the fluctuations become smaller.

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TABLES

Table 1. Provenance table of the compounds used

Name	CAS	Provider	Purity (weight fraction)	Water content (weight fraction)	Purification method
1-propanol	71-23-8	Merck	>0.995	<0.001	none
1-butanol	71-36-3	Merck	>0.995	<0.001	none
cyclohexane	110-82-7	Merck	>0.995	<0.001	none
2-methylpropan-2-ol/ tert-butanol	75-65-0	VWR	>0.999	<0.001	none
K_2SO_4/potassium sulfate	7778-80-5	VWR	>0.997		none
Na_2SO_4/sodium sulfate	7757-82-6	Merck	>0.99		none

Table 2. Boiling temperature of the pure compounds (Tb), phase composition (mole fraction) of the binary azeotrope with water, boiling temperature of the azeotrope (Tb az), phase density and the difference between them ($\Delta\rho$), and the interfacial tension (σ). [15 - 19].

Component	Tb[16]	Phase composition[15]		Tb az	Density ($\rho^{Tb\ az}$)[17] (kg/m^3)		$\Delta\rho$[17]	σ[16]
	(K)	x_1^{org}	x_1^{aq}	(K)	ρ^{org}	ρ^{aq}	(kg/m^3)	(N/m)
1-Butanol	390.9	0.362	0.021	365.4[18]-366.3[18]	800.5	940.9	140.4	0.0015
Cyclohexane	353.9	0.997	0.0001	342.2[19]-342.6[18]	731.7	977.6	245.9	0.0497

Table 3. Vapor phase composition (mole fraction) and standard deviation of the heterogeneous azeotrope water + 1-butanol at 101.3 kPa and a boiling temperature of 365.7 K.

	Bibliography [18]	Without Ultrasound	With Ultrasound
$x_{1\text{-butanol}}$	0.250	0.251	0.250
Standard Deviation		0.027	0.011

The standard uncertainties of the boiling temperature and pressure are 0.06 K and 0.1 kPa respectively.

Table 4. Vapor phase composition (mole fraction) and standard deviation of the heterogeneous azeotrope water + cyclohexane at 101.3 kPa and a boiling temperature of 342.4 K.

	Bibliography [18]	Without Ultrasound	With Ultrasound
$x_{cyclohexane}$	0.701	0.557	0.698
Standard Deviation		0.258	0.036

When ultrasound is applied the standard uncertainties of the boiling temperature and pressure are 0.1 K and 0.1 kPa respectively. When ultrasound is not applied the standard uncertainties of the boiling temperature and pressure are 0.3 K and 3 kPa respectively

Table 5. SLLV, LLV, SLV and LV equilibrium data (mole fraction) of the water + Na_2SO_4 + 2-methylpropan-2-ol system at 101.3kPa

	Solid	Liquid phase I		Liquid phase II		Vapor phase
T/K	Na_2SO_4	Na_2SO_4	2-methylpropan-2-ol	Na_2SO_4	2-methylpropan-2-ol	2-methylpropan-2-ol
			SLLV			
353.18	1	0.000079	0.486	0.0505	0.00105	0.583
			LLV			
353.23		0.000075	0.470	0.0454	0.00140	0.577
353.30		0.000152	0.445	0.0378	0.00378	0.573
353.34		0.000108	0.436	0.0363	0.00297	0.577
353.46		0.000132	0.402	0.0277	0.0063	0.573
353.52		0.000125	0.388	0.0244	0.0066	0.561
353.60		0.000222	0.351	0.0179	0.0123	0.561
353.91		0.00080	0.217	0.00435	0.0479	0.549
			SLV			
353.16	1	0.0000366	0.489			0.587
353.09	1	0.0000127	0.521			0.637
352.95	1	0.00000145	0.669			0.685
			LV			
354.20		0.00306	0.0463			0.580
354.99		0.00250	0.0347			0.562
354.12		0.00244	0.0580			0.566
354.47		0.00347	0.0368			0.549
353.99		0.00272	0.0662			0.550
354.33		0.00220	0.0472			0.546
354.71		0.00298	0.0349			0.551

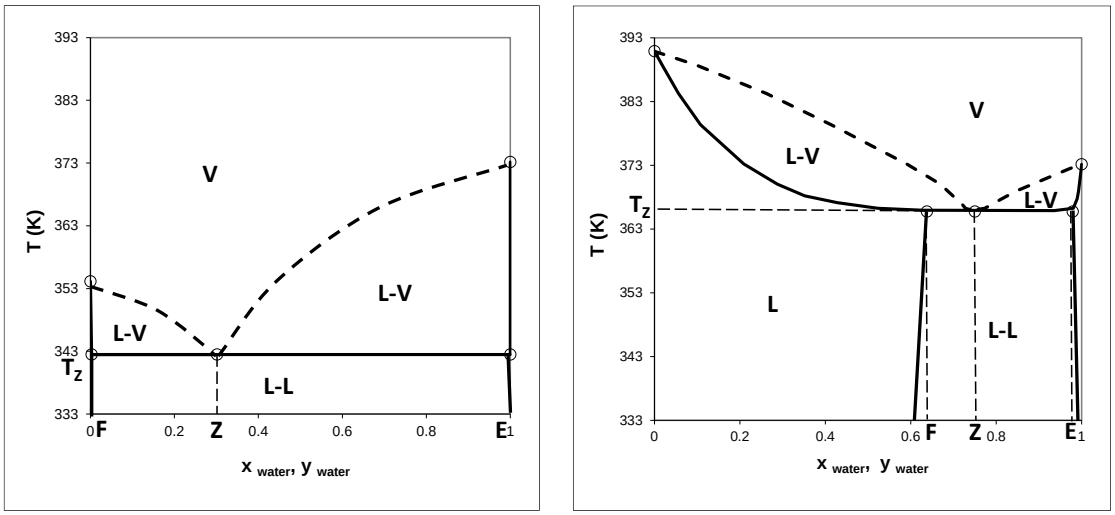
T is in K with a standard uncertainty of 0.06 K, the pressure standard uncertainty is 0.1 kPa and the composition relative standard uncertainty, $u_r = \frac{u}{x}$ is 0.02 except for the Na_2SO_4 in liquid phase I where the relative standard uncertainty is 0.05.

Table 6. SLLV, LLV, SLV and LV equilibrium data (mole fraction) of the water +K_2SO_4 + 2-methylpropan-2-ol system at 101.3 kPa.

	Solid	Liquid phase I		Liquid phase II		Vapor phase
T/K	K_2SO_4	K_2SO_4	2-methylpropan-2-ol	K_2SO_4	2-methylpropan-2-ol	2-methylpropan-2-ol
			SLLV			
353.59	1	0.000215	0.324	0.0137	0.0131	0.560
			LLV			
353.62		0.000210	0.322	0.0135	0.0130	0.560
353.66		0.000298	0.303	0.0111	0.0165	0.560
353.69		0.000282	0.295	0.0102	0.0190	0.560
353.72		0.000322	0.281	0.0088	0.0217	0.559
353.75		0.000398	0.269	0.0077	0.0262	0.559
353.75		0.000343	0.257	0.0069	0.0298	0.559
353.79		0.00056	0.242	0.0058	0.0326	0.558
353.85		0.00078	0.221	0.00497	0.0387	0.558
353.90		0.00090	0.188	0.00350	0.0541	0.558
353.90		0.00117	0.152	0.00291	0.0602	0.555
353.90		0.00112	0.143	0.00253	0.0717	0.554
			SLV			
353.56	1	0.000166	0.335			0.569
353.42	1	0.000099	0.390			0.574
353.14	1	0.0000432	0.473			0.588
352.92	1	0.0000403	0.577			0.617
352.86	1	0.0000350	0.671			0.656
353.05	1	0.0000370	0.758			0.715
353.57	1	0.0000235	0.854			0.796
353.69	1	0.0000237	0.866			0.812
			LV			
356.92		0.0052	0.0106			0.502
359.11		0.00426	0.0074			0.473
362.59		0.0098	0.00248			0.395
358.26		0.00229	0.0109			0.484
356.86		0.0053	0.0111			0.510
357.71		0.0067	0.0084			0.499
355.02		0.000485	0.0294			0.545
354.39		0.00236	0.0292			0.545
353.96		0.00472	0.0259			0.554

T is in K with a standard uncertainty of 0.06 K, the pressure standard uncertainty is 0.1 kPa and the composition relative standard uncertainty, $u_r = \frac{u}{x}$ is 0.02 except for the K_2SO_4 where the relative standard uncertainty is 0.05.

FIGURES



(a) Water + Cyclohexane System (b) Water + 1-Butanol System

Figure 1. Txy diagram (mole fraction) for the heterogeneous binary systems water+1-butanol and water+cyclohexane.

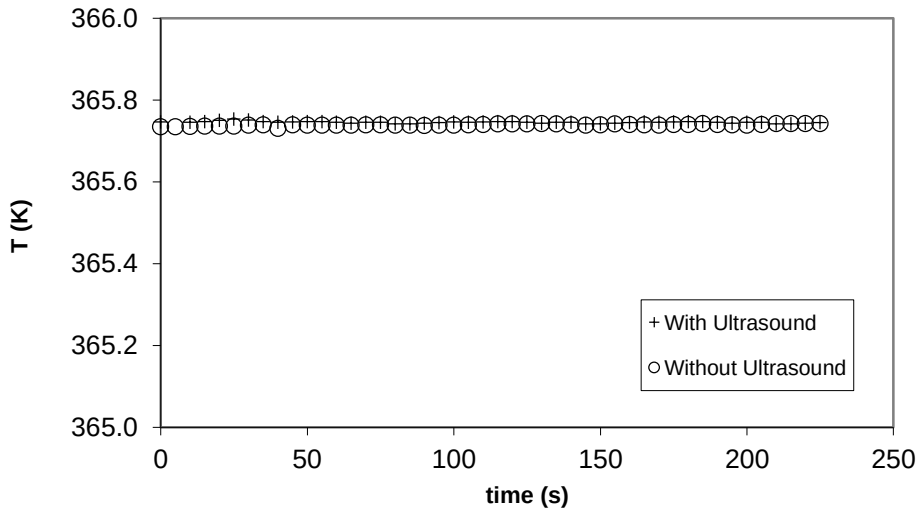


Figure 2. Temperature variation during the determination of the heterogeneous azeotropic point of the water + 1-butanol binary system.

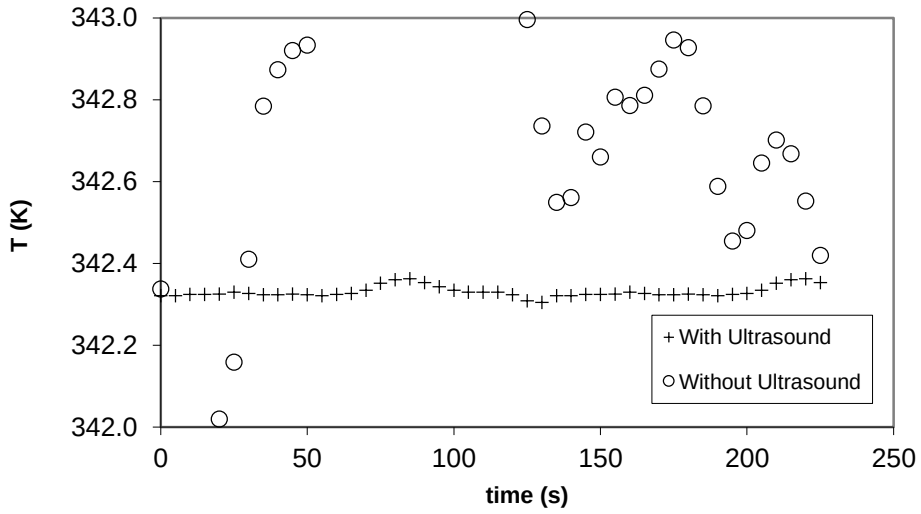


Figure 3. Temperature variation during the determination of the heterogeneous azeotropic point of the water + cyclohexane binary system.

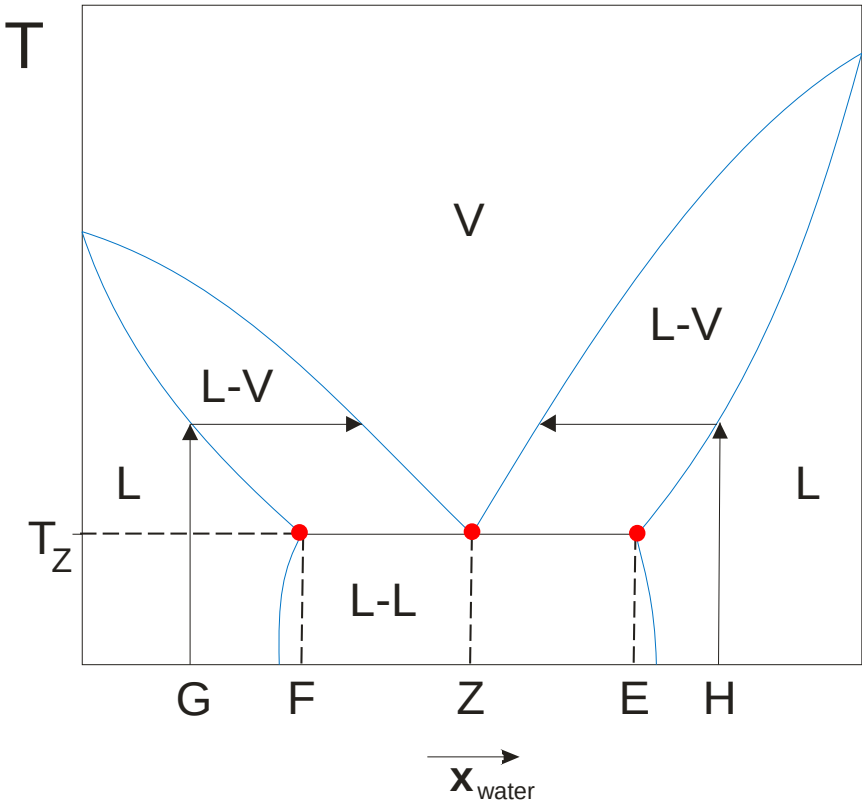


Figure 4. Qualitative Txy diagram for a heterogeneous binary system.

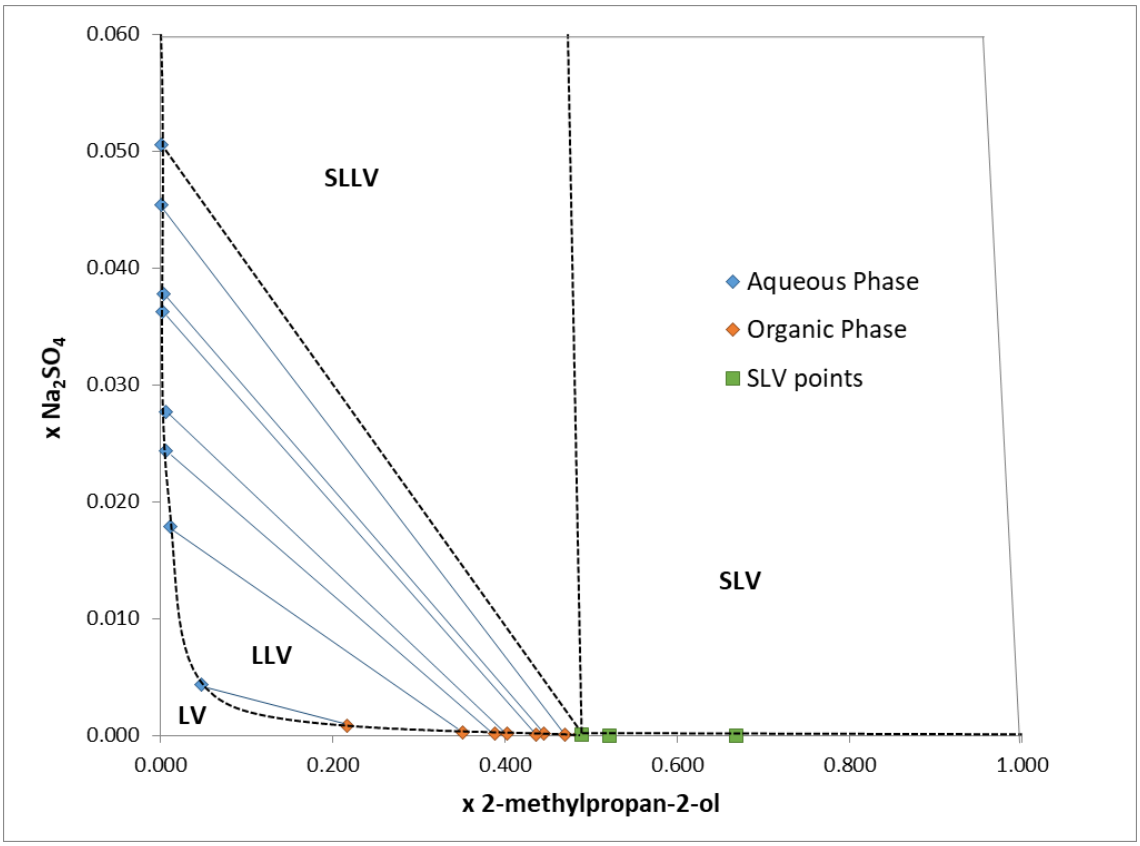


Figure 5. Equilibrium regions of the water + Na_2SO_4 +2-methylpropan-2-ol at boiling temperatures and 101.3 kPa.

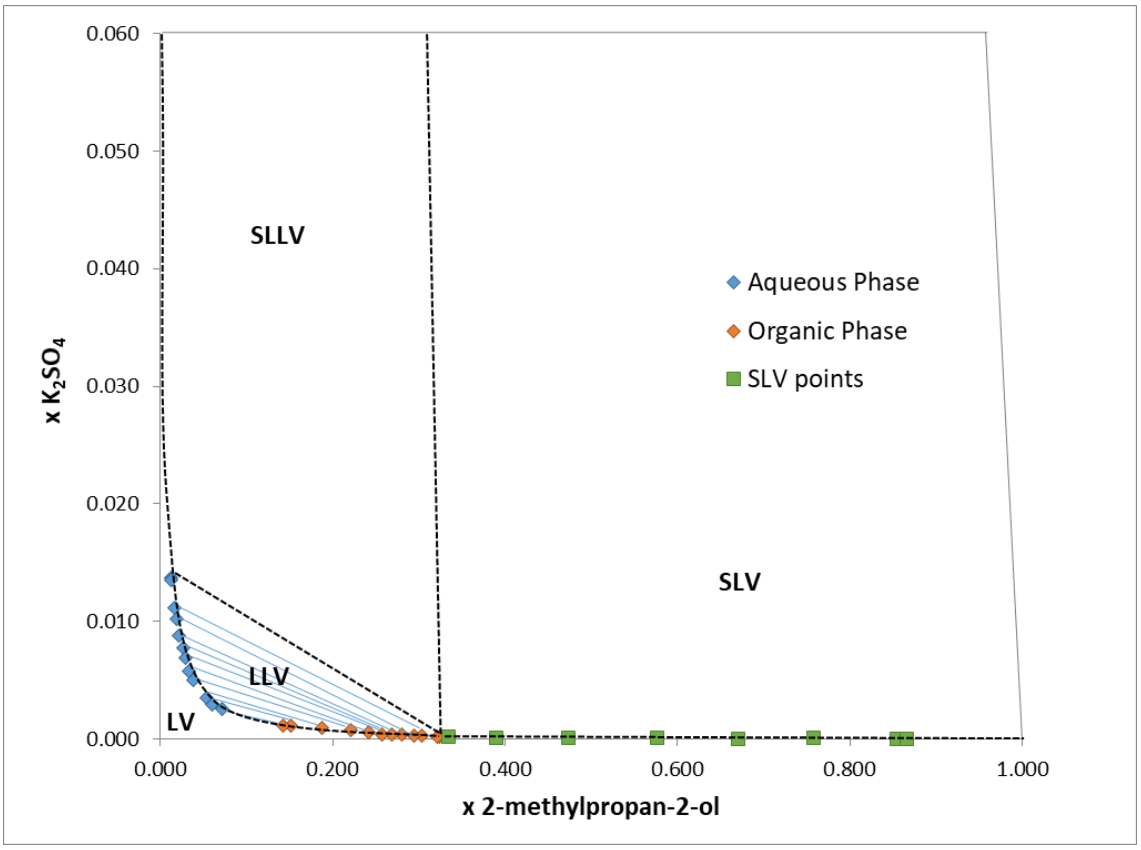


Figure 6. Equilibrium regions of the water + K_2SO_4 +2-methylpropan-2-ol at boiling temperatures and 101.3 kPa.

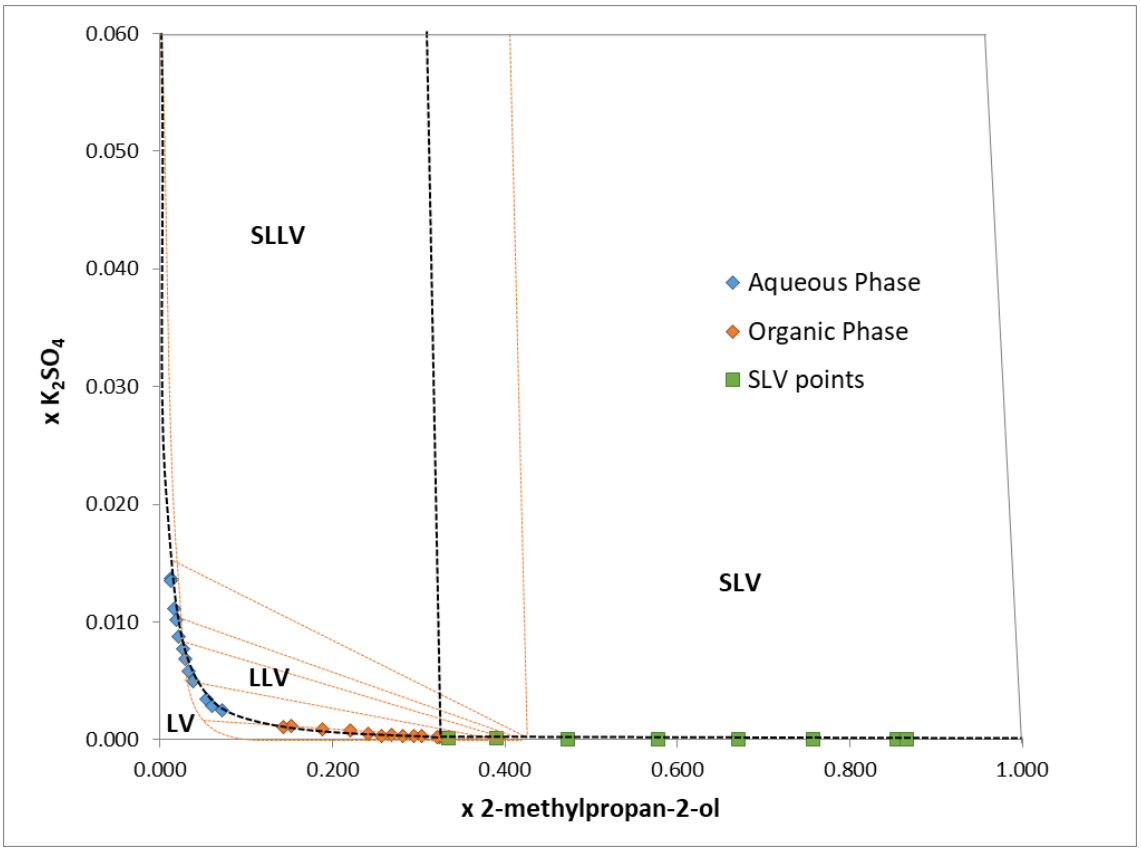


Figure 7. Experimental and calculated equilibrium diagram for the water + K_2SO_4 +2-methylpropan-2-ol at boiling temperatures and 101.3 kPa. -------- Calculated regions by using the modified UNIQUAC model [25].